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Declaration under Rule 4.17:
— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations*

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(54) Title: VANADIUM CATALYSTS AND PROCESS FOR THE DIRECT CONVERSION OF METHANE INTO ACETIC ACID

(57) Abstract: The invention consists on the utilization of complexes of vanadium (in the +4 and +5 oxidation states) with bi- or poly-dentate ligands coordinated by nitrogen and oxygen (N,O) or by oxygen and oxygen (O,O) atoms, namely derivaties of aminoalcohols, (hydroxyimino)dicarboxylic acids, hydroxypyranones, trifluoroacetic acid, triflic acid or inorganic acid, as catalysts for the direct single-pot conversion, under mild conditions, of methane in acetic acid, either in the absence or in the presence of carbon monoxide, and in the presence of a peroxodisulfate salt (K2S2O8), in trifluoroacetic acid (CF3COOH), according to the general reaction (I).

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AMENDED CLAIMS

[Received by the International Bureau on 02 September 2004 (02.09.2004) ; original claims 1 – 4, replaced by amended claims 1 – 3]

1 - Catalyst system and process for the direct one-pot conversion of methane into acetic acid, under

relatively mild conditions, characterized by containing a vanadium complex, a peroxodisulfate salt and trifluoroacetic acid, without requiring the use of carbon monoxide.

2 - Catalyst system and process according to claim 1, characterized by the use of a vanadium complex with the metal in the +4 or +5 oxidation state and with di- or poly-dentate ligands coordinated by nitrogen and/or oxygen atoms namely derived from aminoalcohols, (hydroxyimino)dicarboxylic acids, hydroxypyrones, trifluoroacetic acid or triflic acid.

3 - Catalyst system and process according to claim 2, characterized by the use of carbon monoxide.

STATEMENT UNDER ARTICLE 19 (1)

Statement under Article 19(1) concerning the amendments to Int. application No. PCT/PT 03/00015 (Int. Publication No. WO 2004/037416 A3)

The claims have been amended in order to unambiguously show that there is *no* overlap with the results published by Taniguchi Y. et al., *Org. Lett.*, 1999,*1*, No.4, 557-559, considered as the document of Category X and cited in the application. In fact our process does *not* require the use of carbon monoxide (CO), in contrast with that published process for which the use of CO is essential. Hence, claim 1 was amended accordingly, by adding "without requiring the use of carbon monoxide".

Moreover, by combining claims 2 and 3 into a single one (amended claim 2) and restricting the catalysts compositions, we assure that all our catalysts are different from those applied in the above publication of Category X which used, as catalysts, the vanadium oxides V_2O_3 and V_2O_5, the vanadate salt $NaVO_3$, the 2,4-pentanedionate (acac) compound $[VO(acac)_2]$ and various heteropolyacids like $H_5PV_2Mo_{10}O_{40}$, $H_7PV_4Mo_8O_{40}$ and $H_5SiVW_{11}O_{40}$. The present system uses, as catalysts, the following types of complexes: (i) oxovanadium(V) complexes of the type [VO(*N*,*O*-L)] [*N*,*O*-L = basic form the triethanolamine $N(CH_2CH_2O^-)_3$ or of *N*,*N*-bis(2-hydroxyethyl)glicine (bicine) $N(CH_2CH_2O^-)_2(CH_2COO^-)$], (ii) the synthetic Amavadine and its models, namely the Ca^{2+} salts of the vanadium(IV) complexes, with *N*,*O* ligands, $[V(HIDPA)_2]^{2-}$ [HIDPA = basic form of 2,2'-(hydroxyimino)dipropionic acid, $^-ON\{CH(CH_3)COO^-\}_2$] and $[V(HIDA)_2]^{2-}$ [HIDA = basic form of 2,2'-(hydroxyimino)diacetic acid, $^-ON(CH_2COO^-)_2$], and (iii) the vanadyl complexes of the type $[VO(O,O\text{-L})_2]$ [*O*,*O*-L = basic form (maltolate) of maltol (3-hydroxy-2-methyl-4-pyrone); dibasic form (heida) of 2-hydroxyethyliminodiacetic acid, $N(CH_2CH_2OH)(CH_2COO^-)_2$; trifluoroacetate ($CF_3COO^-$); triflate ($CF_3SO_2O^-$)].

The previous claim 4 (amended claim 3) has been amended accordingly. Although it refers to the use of carbon monoxide, it concerns the use of catalysts (according to amended claim 2) that are different from those of the above publication of category X, as indicated in the previous paragraph concerning the amended claim 2.